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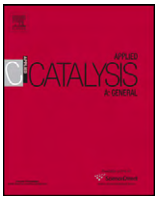

Activation of trimethylsilyl cyanide and mechanistic investigation for facile cyanosilylation by solid acid catalysts under mild and solvent-free conditions

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ABSTRACT

Sulfated-zirconia is found to be a highly efficient heterogeneous solid catalyst in activating trimethylsilyl cyanide (TMSCN) for facile cyanosilylation of aldehydes. A unifying explanation is provided for the cyanosilylation reactions. The unique role of sulfated-zirconia consists of rendering cyanide anions from TMSCN to C=O of aldehydes and providing the corresponding cyanohydrin silyl ethers in quantitative yields under mild and solvent-free conditions.

1. Introduction

Trimethylsilyl nucleophiles (Me_3SiNu) with silicon atoms attached to carbon, nitrogen, oxygen, or sulfur atoms have long been recognized as effective alternatives for proton nucleophiles (HNu) in addition reactions to electrophiles such as aldehydes, ketones, imines, oxiranes, aziridines, nitrones and polar conjugated systems [1]. The number of examples of such additions has been growing steadily over the past 40 years, while the availability of trimethylsilyl nucleophiles is on the rise and new methods of transformation of silylated pronucleophiles into active nucleophiles are emerging. The interest in Me_3SiNu additions was stimulated by the properties of the silicon atom, allowing the generation of active nucleophilic species (Nu^-) under different conditions in comparison to HNu sources. Among all the trimethylsilyl nucleophiles, TMSCN is the best source [2–5], in view of the fact that the average dissociation energy of Si–C bond is extremely low. Trimethylsilyl ethers can readily be isolated or transformed into cyanohydrins by mild acidic hydrolysis. However, cyanohydrins and their trimethylsilyl ethers are key building blocks for one-step synthesis of many biologically active compounds [6–8], ferroelectrics and liquid crystals [9] that are otherwise only obtained with difficulty. They can easily be converted into various functionalized α-hydroxy acids, α-hydroxy aldehydes, β-amino alcohols, α-cyano ketones, 1,2-diols and other polyfunctional compounds [7,10,11]. Because of their importance in organic synthesis and life science research, a large body of work has been devoted to the development of cyanohydrin synthesis. Transfer of a cyano group from TMSCN to an aldehyde/ketone can be catalyzed by numerous reagents [12–21], including Lewis acids, Lewis bases, metal alkoxides, bifunctional catalysts and inorganic salts. Also a few supported versions or versions based on room temperature cyanosilylation reactions [22], activation of TMSCN by N-heterocyclic carbenes [23], solvent-free cyanosilylations [13,24], and mechanistic studies for cyanosilylations have recently been described [25]. However, no zirconia-based solid acid catalyzed activation of trimethylsilyl cyanide for the facile cyanosilylation version has so far been reported. We are currently exploring application of zirconia-based solid acid catalysts to organic syntheses because of numerous advantages [26–30].

In recent years, there has been increasing emphasis on the design and application of environmental friendly solid acid catalysts to reduce the quantity of toxic wastes. Zirconia-based solid acid catalysts are finding outstanding applications as active adsorbents for various gases and for distraction of hazardous chemicals, and as catalysts for many organic transformations [31–34]. More recently, a concerted study from Japan confirmed the superacidity of the sulfated-zirconia catalysts [35]. Recently, we have reported our finding of an efficient zirconia-based solid acid catalyzed Strecker reaction by TMSCN to α-aminonitriles and 1,3-asymmetric induction in Strecker synthesis towards optical active α-aminonitriles [36]. As part of our continued efforts [26–30,36,37] and to gain more insight into this unprecedented mode of reactivity of promoted zirconia-based solid acids, we now wish to disclose a

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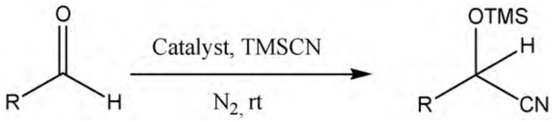


Scheme 1. Well-designed zirconia-based solid acid catalysts for synthesis of trimethylsilyl ethers by using TMSCN under solvent-free conditions.

facile solid acid catalyzed cyanosilylation reaction between TMSCN and aldehydes under mild and solvent-free conditions by activating TMSCN and aldehydes (Scheme 1). This reaction serves as a good example to show that a silicon-based reagent such as TMSCN can be activated by zirconia-based solid acid catalysts for nucleophilic addition reactions. In this work, we synthesized zirconia-based solid acid catalysts and investigated the cyanosilylation of various aldehydes under solvent-free conditions at ambient temperature. The reaction mechanism has also been investigated in detail to understand the role of sulfated-zirconia catalyst by different characterization techniques.

2. Experimental section

2.1. Catalyst preparation

Zirconium hydroxide was prepared first from zirconium oxychloride by hydrolysis with dilute aqueous ammonia solution. For this purpose, the requisite quantity of $ZrOCl_2{\cdot}8H_2O$ (Loba Chime, GR grade) was dissolved in doubly distilled water. To this clear solution, aqueous NH_3 was added dropwise with vigorous stirring until the pH of the solution reached 8. The obtained precipitate was washed with hot distilled water several times until free from chloride ions and dried at 393 K for 24 h. On the resulting hydrous zirconium hydroxide, sulfate, molybdate and tungstate promoters were deposited by a wet impregnation method. To incorporate these promoters, we used sulfuric acid, ammonium heptamolybdate and ammonium metatungstate (Aldrich, AR Grade) as the precursors, respectively. Detailed procedures for the preparation of these catalysts could be found elsewhere [26–30,36,37].

2.2. Catalyst characterization

The powder X-ray diffraction (XRD) patterns of the synthesized catalysts were recorded on a Siemens D-5000 diffractometer by using Cu Kα radiation source and a scintillation counter detector. The XRD phases present in the samples were identified with the help of Powder Diffraction File-International Center for Diffraction Data (PDF-ICDD). The FTIR spectra were recorded on a Nicolet 740 FTIR spectrometer, using KBr discs, with a nominal resolution of 4 cm^{-1} and averaging 100 spectra. The BET surface areas were determined by N_2 physisorption at liquid-N_2 temperature on a Micromeritics Gemini 2360 instrument. Prior to analysis, the samples were oven dried at 393 K for 12 h and flushed with Argon gas for 2 h. Raman spectra were recorded at ambient temperature on a DILOR XY spectrometer equipped with a CCD detector. The spectra were recorded in the range of 4000–100 cm^{-1} and at a spectral resolution of 2 cm^{-1} using the 514.5 nm excitation line from an argon ion laser (Spectra Physics, USA). The temperature programmed desorption (TPD) measurements were carried out on an Auto Chem 2910 instrument (Micromeritics, USA). A thermal conductivity detector was used for continuous monitoring of the desorbed ammonia; the areas under the peaks were integrated using GRAMS/32 software. Prior to TPD studies, samples were pretreated at 473 K for 1 h in a flow of ultra pure helium gas (40 ml min^{-1}). After pretreatment, the sample was saturated with 10% ultra pure anhydrous ammonia gas (balance He, 75 ml min^{-1}) at 353 K for 2 h and subsequently flushed with He (60 ml min^{-1}) at 373 K for 2 h to remove the physisorbed ammonia. The heating rate for the TPD measurements, from ambient to 1023 K, was 10 K min^{-1}. The scanning electron microscopy (SEM) analysis was carried out with a Hitachi model-520 instrument. The finely powdered samples were mounted on a silver sample holder with the help of an adhesive to make the sample surface conductive and were coated with gold metal at 10 mm Hg pressure. X-ray photoelectron spectroscopy (XPS) measurements were conducted with a Kratos Axis 165 instrument with a dual anode (Mg and Al) apparatus using the Mg Kα source. The carbon 1 s binding energy (283.7 eV) was used as reference for determining the binding energies.

2.3. Activity studies

All chemicals employed in this study were commercially available and were used without further purification. A mixture of aldehyde (1 mmol), TMSCN (1.2 mmol) and sulfated-zirconia (SO_4^{2-}/ZrO_2) solid acid catalyst (50 mg) was stirred at room temperature for an appropriate time under N_2 atmosphere. *Caution*: TMSCN must be used in a well-ventilated hood due to its toxicity and moisture sensitive nature. After completion of the reaction, as indicated by TLC, the reaction mixture was filtered and washed with ethyl acetate (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuum and purified by column chromatography on silica gel using ethyl acetate and hexane as eluent to afford pure trimethylsilyl ethers. All products were identified by comparing their spectral data with that in the literature [18,22,24,38].

3. Results and discussion

Incorporation of various promoters (sulfate, molybdate and tungstate) into $Zr(OH)_4$ gel during synthesis showed a strong influence on the bulk and surface properties of the zirconia. XRD and Raman spectroscopy results revealed that addition of promoters enhance tetragonal zirconia phase and surface acidity [37]. Ammonia-TPD results indicated that impregnated sulfate ions show a strong influence and enhance the acidity of zirconia, which is followed by molybdate promoter [37].

At the beginning, we initiated our investigation with the screening of various catalysts by making use of different solvents, varying the amount of catalyst, and using different catalysts obtained by varying the calcination temperature and preheating temperature during synthesis of catalysts. We selected foremost a commonly used aldehyde, benzaldehyde, for cyanosilylation. The results obtained are summarized in Table 1. Preliminary experiments in various solvents revealed that reaction progresses very well under solvent-free conditions (Table 1, Entries 4 and 5) in comparison to the results for different solvents, namely, CH_3CN, $CH_2CH_2Cl_2$ and THF (Table 1, Entries 1–3). Indeed, sulfated-zirconia (SO_4^{2-}/ZrO_2) was found to be more efficient than molybdated-zirconia (MoO_x/ZrO_2) and tungstated-zirconia (WO_x/ZrO_2) catalysts (Table 1, Entries 4, 9, and 10). The calcination temperature of the catalyst also caused a divergence in the yield of the product (Table 1, Entries 11 and 12). Furthermore, an increase in the amount of catalyst showed a significant increase in the yield of the products (Table 1, Entries 5–8). Of course, we could not observe any conversion in the absence of catalyst (Table 1, Entry 14), even after stirring for few days. Similar observation of no activity in the absence of catalyst and influence of other parameters was also made earlier in the literature under identical reaction conditions identical to these employed in the present study [5]. These results clearly emphasize the role of promoted zirconia catalyst.

Table 1
Search for optimal catalysts and reaction conditions[a].

Sr. no.	Catalyst	Amount of catalyst (mg)	Solvent	Time (min)	Yield (%)[b]	BET SA ($m^2 g^{-1}$)	NH_3 desorbed (ml/g)
1.	SO_4^{2-}/ZrO_2	50	ACN	120	56	100	16
2.	SO_4^{2-}/ZrO_2	50	EDC	120	62	100	16
3.	SO_4^{2-}/ZrO_2	50	THF	120	25	100	16
4.	SO_4^{2-}/ZrO_2	50	–	120	67	100	16
5.	SO_4^{2-}/ZrO_2[c]	50	–	120	82	100	16
6.	SO_4^{2-}/ZrO_2	40	–	120	55	100	16
7.	SO_4^{2-}/ZrO_2	30	–	120	43	100	16
8.	SO_4^{2-}/ZrO_2	20	–	120	36	100	16
9.	WO_3/ZrO_2	50	–	120	55	94	09
10.	MoO_3/ZrO_2	50	–	120	59	35	11
11.	SO_4^{2-}/ZrO_2[d]	50	–	120	76	–	–
12.	SO_4^{2-}/ZrO_2[e]	50	–	120	88	–	–
13.	SO_4^{2-}/ZrO_2	50	–	90	~100[f]	100	16
14.	–	–	–	–[g]	NR	–	–

NR: no reaction.

[a] Reagents and reaction conditions; benzaldehyde (1 mmol) TMSCN (1.2 mmol), 2 ml solvent.

[b] Yields evaluated by ^1H NMR spectroscopy.

[c] Preheating at 523 K.

[d] Calcination at 973 K.

[e] Calcination at 1073 K.

[f] Reaction of 90 min.

[g] Seven days.

In order to examine the possibility of recyclability, after the reaction we removed the solid catalyst conveniently by simple filtration from the reaction mixture. The wet catalyst was reused for next reaction without any washing. Each catalyst could be easily recovered and reused for at least 5 cycles with trivial changes in the catalytic activity. Recycling experiments were examined for the cyanosilylation of benzaldehyde at room temperature (Fig. 1).

With these "green" conditions in hand, we then explored the scope of this new promoted zirconia-based solid acid catalyzed cyanosilylation reaction (Scheme 1 and Table 2). We also investigated the role of aldehyde in this reaction. Aromatic aldehydes having electron withdrawing and donating substituents, heteroaromatic and vinyl aldehydes are found to be active for cyanosilylation reaction with sulfated-zirconia offering good to better yields (62–96%) within short reaction times (50–200 min). Moreover, the reaction conditions are mild enough to perform the reaction in the presence of acid sensitive substrates, such as furfuraldehyde and cinnamaldehyde without any decomposition or polymerization (Table 2, Entries 6 and 10). In the meantime, we also investigated the role of a catalyst to activate TMSCN and aldehydes towards cyanosilylation reactions.

3.1. Mechanistic investigation

Recent studies suggest that the activation of n-butane for isomerization of alkanes, the activation of CO for carbonylation of benzene and methane, and the activation of alkanes for alkene formation are promoted by adsorption on the sulfated-zirconia catalyst [39–42]. Based on these reports, we contemplated that trimethylsilyl cyanide could be activated by adsorption on the sulfated-zirconia solid acid catalyst for cyanosilylation of aldehydes.

Spectroscopic studies were used to understand the interactions between trimethylsilyl cyanide and the surface of the sulfated-zirconia catalyst. From the studies of metal cyanide complexes and the cyanide adsorbed on the metal surfaces by using electron energy-loss spectroscopy (EELS), XPS and other techniques, it has been proposed that the linear coordination (σ bonding) through the lone-pair electrons of the nitrogen atom results in an increase of the C≡N stretching frequency compared with that of the free trimethylsilyl cyanide molecule [43,44]. We investigated the adsorption of TMSCN and benzaldehyde on the surface of sulfated-zirconia by using FTIR (Fig. 2) and XPS techniques (Fig. 3). In the FTIR spectra, the C≡N stretching was observed at 2189 cm^{-1} for free TMSCN molecules, which is consistent with the reported values [45,46]. When sulfated-zirconia was immersed in the TMSCN solution and then the residue was filtered off, rinsed with chloroform, and analyzed by FTIR spectroscopy, the peak of the C≡N stretching appeared at 2338 cm^{-1}. The C≡N stretching band was blue-shifted by 149 cm^{-1}. The blue shift indicate the adsorption and interaction of TMSCN on the surface of sulfated-zirconia, and the linear coordination (σ bonding) through the lone-pair electrons of the nitrogen atom results in an increase of the C≡N stretching frequency compared with that of the free trimethylsilyl cyanide molecule. In other words, the blue shift can be attributed to the effect of nitrogen to metal cation (Zr^+) electron donation. Notably, the stretch of the cyanide anion in water occurs at 2080 cm^{-1} and the coordination of the anion at a metal always increases the frequency of this absorption [47]. This phenomenon suggests that the cyanide ligand has significantly interacted with the Zr^{4+} ions, which are Lewis acidic centres on the surface of the catalyst. We perceive a strong absorption band in the range of 900–1300 cm^{-1}. It is suggested that this band is the result of superimposition of two absorption peaks. One is the strong 1156 cm^{-1} peak attributed to the Zr–N stretching vibration, suggesting that there may be an electronic change from nitrogen to Zr^+ Lewis acidic center. Comparison with other oxides leads us to suggest that the cationic charge borne by the metallic cation is of prime importance for the acid strength in the catalyst [48]. The other is the 1213 cm^{-1} line caused by the C–N and Si–CH_3 stretching vibration [49]. There are

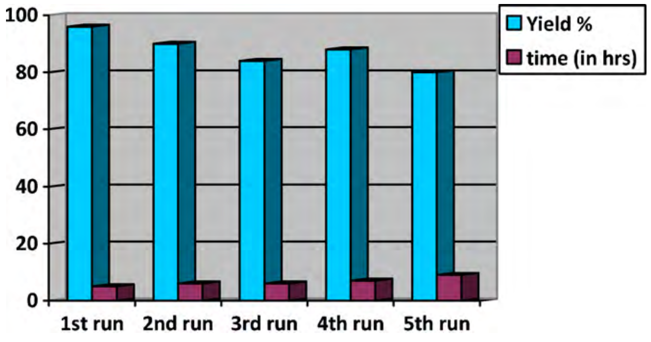
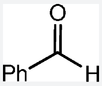
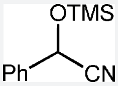
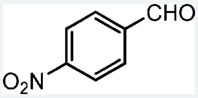
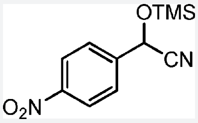
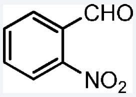
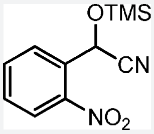
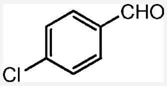
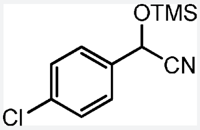
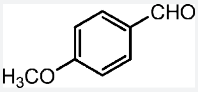
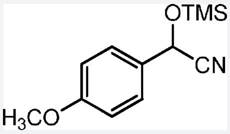
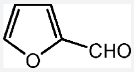
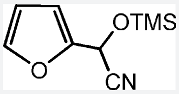
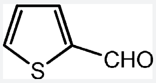
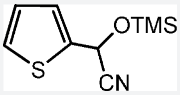
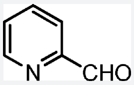
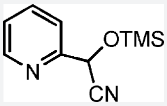
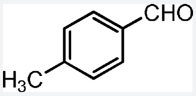
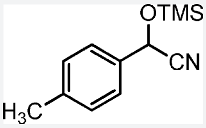
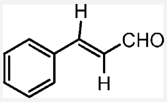
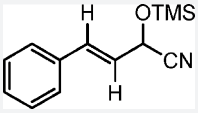


Fig. 1. Recyclability of SO_4^{2-}/ZrO_2 catalyst.

Table 2
Cyanosilylation of a variety of aldehydes in presence of SO_4^{2-}/ZrO_2[a].

Entry	Aldehyde	Product	Time (min)	Yield (%)[b]
1.			300	96
2.			100	88
3.			150	81
4.			90	93
5.			200	91
6.			50	92
7.			65	87
8.			90	95
9.			120	86
10.			70	75

[a] Reagents and reaction conditions; aldehyde (1 mmol), TMSCN (1.2 mmol) under N_2 atmosphere at room temperature.
[b] Isolated yields of pure products.

no peaks observed at ~1500 cm^{-1} and ~2100 cm^{-1}, which would be attributed to N–H bending and Si–H stretching, suggesting that there is no transfer of hydrogen from sulfated-zirconia to TMSCN. The peak at 700–800 cm^{-1} is attributed to Si–C stretching or Si–CH_3 rocking or wagging [50].

The IR spectra of the sulfated-zirconia immersed in the benzaldehyde solution and taken out, and rinsed with chloroform contained an absorption peak at 1686 cm^{-1} that could be attributed to the chemisorption of aldehyde on the surface of sulfated-zirconia catalyst. The C=O stretching frequencies at 1698 cm^{-1} and 1686 cm^{-1} correspond to physisorbed and chemisorbed benzaldehyde [22], respectively. Note that the spectrum of neat benzaldehyde also displays a carbonyl stretching band at 1698 cm^{-1}, which suggests that the benzaldehyde is chemisorbed on the catalyst surface and that the catalyst is activating both aldehyde and TMSCN.

The results for sulfated-zirconia were partly obscured by an intense band at 1392 cm^{-1} due to a vibration of sulfate groups. However, the dominant detectable mode of adsorption involved grafting of trimethysilylcyano groups to Lewis acidic exposed Zr^{4+} sites at 2338 cm^{-1}. Trimethylsilyl cyanide would be expected to be protonated at strongly Brønsted acidic sites on the sulfated-zirconia, but we did not observe any peak related to the same. No change in the color of the pressed discs in the present IR cell was observed when trimethylsilyl cyanide was adsorbed on the sulfated-zirconia. This could be taken as evidence for no proton transfer from the catalyst to the TMSCN. Colour change and FTIR results remain as definite indicators of no protona-

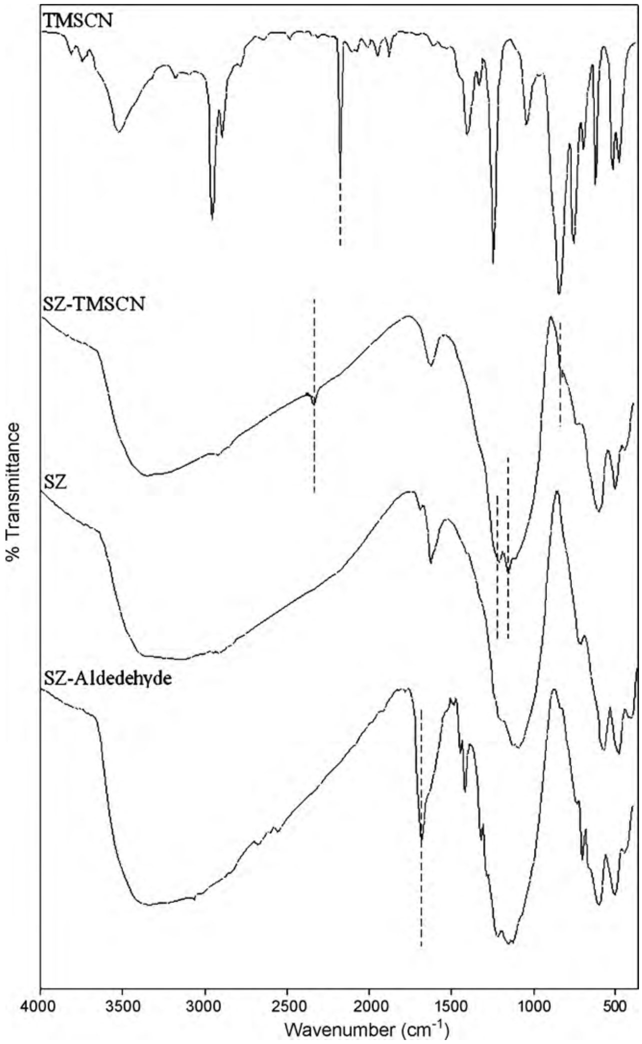


Fig. 2. FTIR spectra of the catalyst before and after reaction: (SZ)–fresh SO_4^{2-}/ZrO_2 catalyst; (SZ–TMSCN)–SO_4^{2-}/ZrO_2 catalyst after reaction with TMSCN; (SZ–aldehyde)–SO_4^{2-}/ZrO_2 catalyst after reaction with aldehyde.

tion occurring during TMSCN adsorption on the sulfated-zirconia. In sulfated-zirconia, the Lewis acidic centers (Zr^+) are generally electron-deficient sites and they are strengthened by the electron-withdrawing nature of the sulfate groups. TMSCN molecules may be adsorbed on sulfated-zirconia either in a flat or perpendicular orientation to the surface. The strong electron-donating character of the CN group donates much electron density to Lewis acidic sites thereby increasing the strength of adsorption at Lewis acidic surface sites *via* interaction with the cyanide in a flat orientation. After high temperature treatments, the sulfated oxide demonstrates mainly Lewis acidity rather than Brønsted acidity [51]. Morterra et al. [52] have elegantly shown that raising the treatment temperature decreases the Brønsted activity and increases the Lewis acidity as monitored by IR spectra of adsorbed pyridine. As already confirmed by IR spectroscopy, the Lewis acidic sites in sulfated-zirconia are activating the TMSCN for cyanosilylation. An attempt has therefore been made here to generate a sulfated-zirconia surface exhibiting a higher level of Lewis acidity than that of the sulfated-zirconia which had been pretreated at 250 °C. Consequently, we carried out the cyanosilylation of aldehyde reaction with TMSCN as a cyanide source by taking the sulfated-zirconia catalyst preheated at 350 °C, and we observed a greater increase in the product yield 67–82% within 45 min (Table 1, Entries 4 and 5). Also, we carried out this reaction by employing sulfated-zirconia catalyst calcined at 650, 700 and 800 °C, and we observed great increments in conversion of aldehydes to cyanosilylated products (Table 1, Entries 11 and 12). These studies prove that activation of TMSCN occurred by the adsorption on the surface of Lewis acidic sites of sulfated-zirconia.

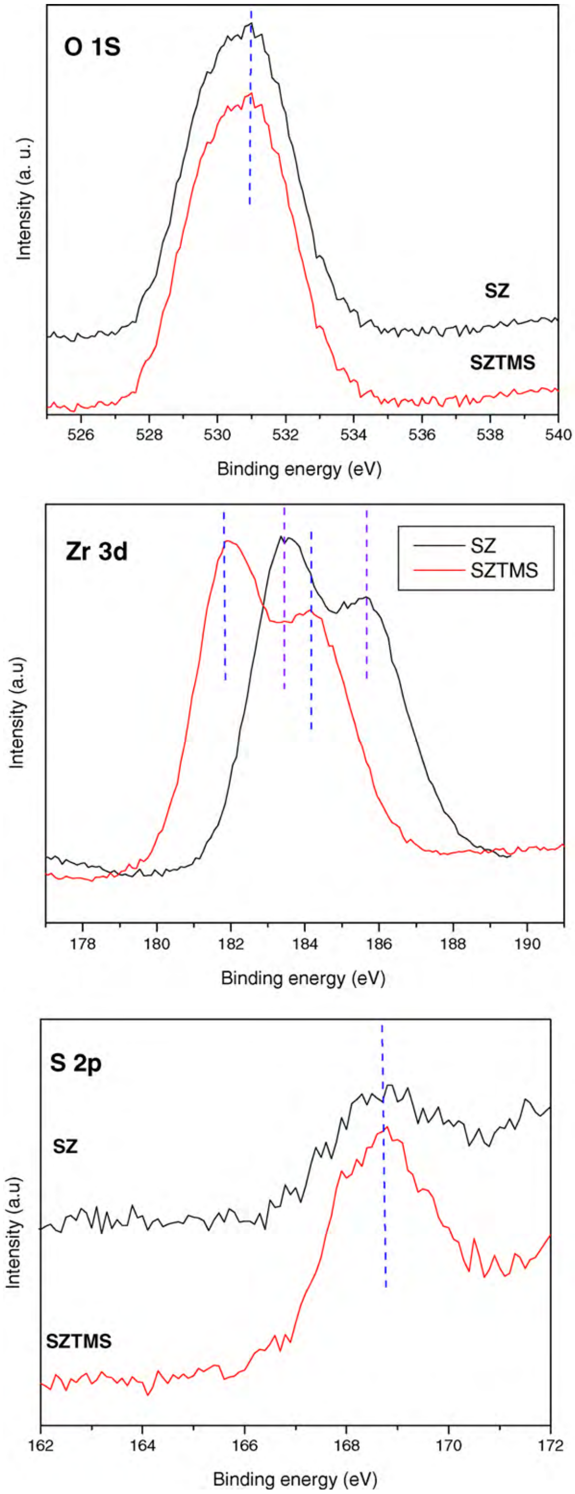
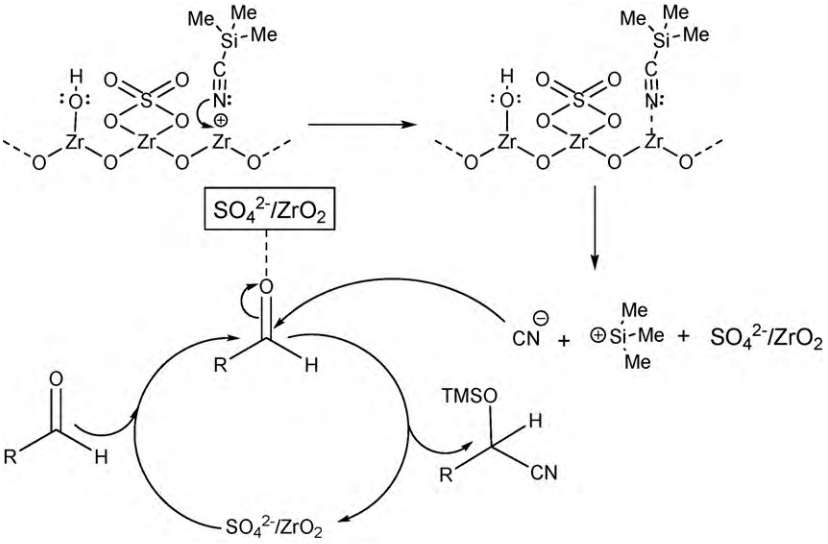


Fig. 3. XPS spectra of the catalysts before and after reaction with TMSCN: (SZ)–fresh SO_4^{2-}/ZrO_2 catalyst; (SZTMS)–SO_4^{2-}/ZrO_2catalyst after reaction with TMSCN.

The chemical compositions of the surface layers of sulfated-zirconia before and after reaction with TMSCN were studied through XPS analysis to understand whether TMSCN is binding on surface Brønsted acid sites or Lewis acid sites. The Zr $3d_{5/2}$ at



Scheme 2. Plausible reaction mechanism for cyanosilylation of aldehydes catalyzed by SO_4^{2-}/ZrO_2.

183.51 eV and Zr $3d_{3/2}$ at 185.60 eV appeared in the XP spectra of sulfated-zirconia sample, but these peaks are shifted to lower binding energies, i.e., Zr $3d_{5/2}$ at 181.92 eV and Zr $3d_{3/2}$ at 184.11 eV in the spectra of TMSCN adsorbed sample (SZTMS). It could be due to changes in electron density around surface zirconium ions, which are electron-deficient Lewis acidic sites as reported earlier in the literature [53]. From the peak of the N 1s corresponding to the SZTMS sample, the peak with a binding energy of 398.00 eV is assigned to Zr–N bond in conformity with the literature [54]. The Si 2p and C 1s peaks were observed at 101.08 eV and 283.63 eV, which are corresponding to the values for SZTMS sample, but these are less intense peaks. There is no shift in the binding energies in the cases of O 1s and S 2p this mean that the cyanide source is interacting only with Lewis acidic sites not with Brønsted sites. XPS results are also supporting the blue shift of cyanide peak in FTIR spectroscopic observations. All these results are tending to support an active role of solid acid and supporting the mechanism presented in Scheme 2 for the formation of cyanosilyl ethers.

The spectral data for some of the selected envoy compounds is given below:

2-Phenyl-2-(trimethylsilyloxy) acetonitrile (Table 2, **Entry 1**): ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.29$ (s, 9H), 5.53 (s, 1H), 7.41–7.58 (m, 5H); FTIR (Neat): ν 3436, 3035, 2960, 1696, 1453, 1255, 1194, 1097, 1071, 853, 752, 696 cm^{-1}; EIMS: *m*/*z* calcd for $C_{11}H_{15}NOSi$ (M^+): 205.

2-(4-Nitrophenyl)-2-(trimethylsilyloxy) acetonitrile (Table 2, **Entry 2**): ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.28$ (s, 9H), 5.61 (s, 1H), 7.65–7.68 (m, 2H), 8.23–8.27 (m, 2H); FTIR (Neat): ν 3427, 2976,1954, 1718, 1453, 1270, 1071, 1018, 761, 709 cm^{-1}; EIMS: *m*/*z* calcd for $C_{11}H_{14}N_2O_3Si$ (M^+): 250.

2-(2-Nitrophenyl)-2-(trimethylsilyloxy) acetonitrile (Table 2, **Entry 3**): ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.29$ (s, 9H), 6.20 (s, 1H), 7.93–8.01 (m, 2H), 8.09–8.14 (m, 2H); FTIR (Neat): ν 3402, 3107, 2960, 1701, 1530, 1348, 1256, 1189, 1109, 1071, 851, 789, 738, 698 cm^{-1}; EIMS: *m*/*z* calcd for $C_{11}H_{14}N_2O_3Si$ (M^+): 250.

2-(4-Cholorophenyl)-2-(trimethylsilyloxy) acetonitrile (Table 2, **Entry 4**): ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.25$ (s, 9H), 5.43 (s, 1H), 7.34–7.41 (m, 4H). FTIR (Neat): ν 3392, 3118, 2042, 1704, 1462, 1340, 1075, 1018, 788, 629 cm^{-1}; EIMS: *m*/*z* calcd for $C_{11}H_{14}ClNOSi$ (M^+): 239.

2-(4-Methoxyphenyl)-2-(trimethylsilyloxy) acetonitrile (Table 2, **Entry 5**): ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.24$ (s, 9H), 2.14 (s, 3H), 5.43 (s, 1H), 7.32–7.42 (m, 2H), 7.47–7.51 (m, 1H), 7.77–7.82 (m, 1H). FTIR (Neat): ν 3342, 3113, 1749, 1605, 1433, 1298, 1220, 1024, 989, 743, 682, 618 cm^{-1}; EIMS: *m*/*z* calcd for $C_{12}H_{17}NO_2Si$ (M^+): 235.

2-Furanyl (trimethylsilyloxy) acetonitrile (Table 2, **Entry 6**): ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.29$ (s, 9H), 5.58 (s, 1H), 6.41–6.43 (m, 1H), 6.57–6.6 (m, 1H), 7.4–7.52 (m, 1H). FTIR (Neat): ν 3390, 3092, 2254, 1723, 1319, 1230, 1054, 864, 759, 656 cm^{-1}; EIMS: *m*/*z* calcd for $C_9H_{13}NO_2Si$ (M^+): 195.

2-Thiophenyl (trimethylsilyloxy) acetonitrile (Table 2, **Entry 7**): ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.22$ (s, 9H), 5.68 (s, 1H), 6.83–6.86 (dd, 1H), 7.02–7.03 (m, 1H), 7.20–7.22(dd, 1H); FTIR (Neat): ν 3403, 3110, 2251,1653, 1419, 1237, 1031, 847, 712, 667 cm^{-1}; EIMS: *m*/*z* calcd for $C_9H_{13}NOSSi$ (M^+): 211.

2-Pyridinyl (trimethylsilyloxy) acetonitrile (Table 2, **Entry 8**): ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.36$ (s, 9H), 5.63 (s, 1H), 7.35–7.40 (m, 1H), 7.66–7.69 (m, 1H), 7.83–7.90 (m, 1H), 8.63–8.67 (m, 1H); FTIR (Neat): ν 3418, 3109, 2925, 2147, 1725, 1597, 1450, 1347, 1297, 1246, 1084, 752, 679, 536 cm^{-1}; EIMS: *m*/*z* calcd for $C_{10}H_{14}N_2OSi$ (M^+): 206.

2-(4-Methylphenyl)-2-(trimethylsilyloxy) acetonitrile (Table 2, **Entry 9**): ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.13$ (s, 9H), 2.27 (s, 3H), 5.49 (s, 1H), 7.18 (d, 2H) 7.25 (d, 2H); FTIR (Neat): ν 3173, 2926, 1741, 1591, 1438, 1283, 1242, 1110, 1048, 998, 752, 702, 619 cm^{-1}; EIMS: *m*/*z* calcd for $C_{12}H_{17}NOSi$ (M^+): 219.

4. Conclusions

In summary, among the promoted zirconia and other solid acid catalysts, sulfated-zirconia is found to be the most efficient for the title reaction. Solvent-free, mild and ambient temperature reaction conditions, experimental simplicity, inexpensive catalyst, high yield of the products and shorter reaction times are some of the advantages associated with this methodology. The FTIR and XP spectroscopic studies suggested that TMSCN is activated for the cyanosilylation of aldehydes by adsorbing on the Lewis acidic sites of the sulfated-zirconia catalyst.

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